

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 074-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 25, 2006	3. REPORT TYPE AND DATES COVERED Final Report 05-01-02 to 12/31/05	
4. TITLE AND SUBTITLE Coherent Quantum Control of Multidimensional Vibrational Spectroscopy			5. FUNDING NUMBERS #FA9550-04-1-0332	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California, Irvine Department of Chemistry 1102 Natural Sciences II Irvine, CA 92697-2025			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 4015 Wilson Blvd., Room 713 Arlington, VA 22203-1954 <i>Dr. Michael Berman</i>			10. SPONSORING / MONITORING AGENCY REPORT NUMBER AFRL-SR-AR-TR-06-0218	
11. SUPPLEMENTARY NOTES Final Report				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 Words) The difference frequency generation (DFG) signal from a two electronic level system with vibrational modes coupled to a Brownian oscillator bath was computed. Simulations of two-dimensional DFG signals illustrated how the ground and excited electronic state resonances may be distinguished. Factorial moments of photon counting statistics from a single molecule coupled to a quantum bath were expressed in terms of multipoint quantum correlation functions and represented by double-sided Feynman diagrams. The results of stochastic models of spectral diffusion where the bath dynamics were independent of the state of the system were recovered and the moments described. Closed expressions for tunneling currents in molecular junctions were derived in electron-phonon coupling. The Keldysh-Schwinger formalism was recast in terms of density matrices in Liouville space. The current was related to the decay of coherences in Fock space between many-body molecular states. Effects of hydrogen-bond forming and breaking kinetics on the linear and coherent third-order infrared spectra were described by Markovian fluctuations and simulated using stochastic Liouville equations. Slow and fast frequency fluctuations were distinguished and described. Recursive relations were developed for computing the multipoint correlation functions of a particle undergoing a biased continuous-time random walk (CTRW) in an external potential. Comparison of the CTRW with the Brownian harmonic oscillator model illustrated how higher-order correlation functions may be used to distinguish between dynamical models that have the same two-point correlation function.				
14. SUBJECT TERMS Coherent Spectroscopy, Four Wave Mixing, Hydrogen Bonds, Photon Statistics, Anomalous Diffusion			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

AFOSR Final Report

**Title: Coherent Quantum Control of Multidimensional
Vibrational Spectroscopy**

Grant Number: #FA9550-04-1-0332

Period of Performance: 05/01/02 to 12/31/05

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20060710039

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Accomplishments/New Findings:

Computer code is being developed for multidimensional signals.

Personnel Supported:

Principal Investigator:

Shaul Mukamel
Frantisek Sanda
Upendra Harbola
Ravi Venkatramani
Dmitri Varonine

Technical Summary:**Dephasing-induced Vibronic Resonances in Difference Frequency Generation Spectroscopy**

The difference frequency generation (DFG) signal from a two electronic level system with vibrational modes coupled to a Brownian oscillator bath was computed. Interference effects between two Liouville space pathways result in pure-dephasing-induced, excited-state resonances provided the two excitation pulses overlap and time ordering is not enforced. Numerical simulations of two-dimensional DFG signals illustrate how the ground and excited electronic state resonances may be distinguished.

Stochastic Liouville Equations for Hydrogen-Bonding Fluctuations and their Signatures in Two Dimensional Vibrational Spectroscopy of Water

The effects of hydrogen-bond forming and breaking kinetics on the linear and coherent third-order infrared spectra of the OH stretch of HOD in D₂O were described by Markovian, not necessarily Gaussian, fluctuations and simulated using the stochastic Liouville equations. Slow (0.5 ps) fluctuations are represented by a collective electrostatic coordinate, whereas fast (100 fs) frequency fluctuations are described using either a second collective electrostatic coordinate or a four-state jump (FSJ) model for hydrogen-bonding configurations. Parameters for both models were obtained using a 1-ns molecular-dynamics trajectory calculated using the TIP4P force field combined with an electrostatic *ab initio* map. The asymmetry of the photon-echo spectra (larger linewidth on the blue side than on the red side) predicted by the FSJ is in better agreement with recent experiments.

Multipoint Correlation Function for Continuous Time Random Walk Models of Anomalous Diffusion

Recursive relations were developed for computing the multipoint correlation functions of a particle undergoing a biased continuous-time random walk (CTRW) in an external potential. Two- and three-point correlation functions were calculated for waiting-time distributions with an anomalous power-law profile $t^{-\alpha-1}$, $0 < \alpha < 1$, on intermediate time scales with a crossover to an exponential long time decay. Comparison of the CTRW with the Brownian harmonic oscillator model (Gaussian process) illustrates how higher-order correlation functions may be used to distinguish between dynamical models that have the same two-point correlation function.

Non-equilibrium Superoperator Greens Function Approach to Inelastic Resonances in STM Currents

Closed expressions for tunneling currents in molecular junctions were derived to fourth-order in electron-phonon coupling. The Keldysh-Schwinger formalism is recast in terms of density matrices in Liouville space, and the calculation only involves forward propagation in real time and is represented by the double sided Feynman diagrams commonly used for computing optical response functions. The current is related to the decay of coherences in Fock space between many-body molecular states with N and $N \pm 1$ electrons. Application is made to the fundamental and overtone vibrational resonances of methane.

Liouville Space Pathways for Spectral Diffusion in Photon Statistics from Single Molecules

The factorial moments of photon counting statistics from a single molecule coupled to a quantum bath were expressed in terms of multipoint quantum correlation functions and represented by double-sided Feynman diagrams, in close formal analogy with nonlinear spectroscopy. At infinite temperature we recover the results of stochastic models of spectral diffusion where the bath dynamics is independent on the state of the system and the moments are described by lower-order correlation functions.

Publications:

1. "Dephasing-induced Vibronic Resonances in Difference Frequency Generation Spectroscopy," R. Venkatramani and S. Mukamel, J. Phys. Chem. B, 109 8132-8143 (2005).
2. "Multipoint Correlation Function for Continuous Time Random Walk Models of Anomalous Diffusion" F. Sanda and S. Mukamel, Phys. Rev. E 72, 031108 (2005).
3. "Non-equilibrium Superoperator Greens Function Approach to Inelastic Resonances in STM Currents", U. Harbola, J. Maddox and S. Mukamel, Phys. Rev. B, 2006 (in press).
4. "Liouville Space Pathways for Spectral Diffusion in Photon Statistics from Single Molecules," F. Sanda and S. Mukamel, Phys. Rev. A, 71, 033807 (2005).
5. "Stochastic Liouville Equations for Hydrogen-Bonding Fluctuations and their Signatures in Two Dimensional Vibrational Spectroscopy of Water" Thomas la Cour Jansen, Tomoyuki Hayashi, Wei Zhuang and Shaul Mukamel, J. Chem. Phys. 123, 114504 (2005).

Interactions/Transitions:

Participation/presentations at meetings, conferences, seminars, etc.:

2004

"Multidimensional Optical Spectroscopies of Molecules and Aggregates: Snapshots of Electronic and Vibrational Coherence", Physical Chemistry Seminar Series, University of Pennsylvania, Philadelphia, PA, February 5, 2004.

"Nonlinear Coherent Electronic and Vibrational Spectroscopy of Molecules: Computational Challenges", Theory and Applications of Computational Chemistry (TACC) Meeting, Gyeongju, Korea, February 15-20, 2004.

"Multidimensional Optical Spectroscopies of Molecules and Aggregates: Snapshots of Electronic and Vibrational Coherence", Symposium on Molecular Reaction Dynamics in Condensed Matter, Laguna Beach, CA, March 3-6, 2004.

"Multidimensional Optical Coherent Spectroscopies of Polypeptides: Femtosecond Snapshots of Vibrational Dynamics", Chemistry Seminar, Wake Forest University, Winston-Salem, NC, March 16-17, 2004.

"Structure, Dynamics, and Hydrogen Bonding Fluctuations of Peptides Probed by Coherent Infrared Multidimensional Spectra", 227th ACS National Meeting, Anaheim, CA March 28-April 1, 2004.

Workshop on Ultrafast x ray Science, San Diego, CA April 28- May 1, 2004.

"Multidimensional Spectroscopies of Vibrational Excitations in Peptides" International Workshop and Seminar on Cooperative Phenomena in Optics and Transport in Nanostructures, Max Planck Institute, Dresden, Germany, May 31-June 25, 2004.

"Coherent Femtosecond Multidimensional Spectroscopies of Excitons", The Center for nonlinear Studies Workshop on Quantum and Semiclassical Molecular Dynamics of Nanostructures, Los Alamos National Laboratory, Albuquerque, NM, July 15-17, 2004.

"Many -Body Approaches to Multidimensional Spectroscopies", 2nd International Conference on Coherent Multidimensional Vibrational Spectroscopy, University of Wisconsin, Madison, WI, August 15-17, 2004.

"Multipoint Fluctuations, Response, and Quantum Extensions of the Jarzynski Relation, Workshop on Stochastic and Deterministic Dynamics, The Erwin Schrödinger International Institute for Mathematical Physics, Vienna, Austria, August 25-28, 2004.

Summer School on Time-Dependent Density-Functional Theory: Prospects and Applications, Barcelona-Benassaque, Spain, August 28-September. 12, 2004.

DOE Atomic Molecular And Optical Sciences Research Meeting, Arlie Conference Center, Warrenton, VA, September, 2004.

"Femtosecond Coherent Optical Response of Vibrational and Electronic Excitons", The First MIT-ENS Cachan Workshop on Molecular Photonics, Massachusetts Institute of Technology, Cambridge, MA, October 10-11, 2004.

"Structure and Dynamical Fluctuations of Peptides Probed by Coherent Infrared Multidimensional Spectra", Frontiers in Optics/Laser Science Conference, Rochester Convention Center, Rochester, NY, October 11-14, 2004.

"Multidimensional Coherent Vibrational Femtosecond Snapshots of Molecular Dynamics", Chemistry Seminar, Arizona State University, Tempe, AZ, November 8, 2004.

"Novel Nanoengineered Chromophore Aggregates with Controlled Electronic and Optical Properties", 2004 Nanoscale Science and Engineering Grantee Conference, Arlington, VA, December 13-15, 2004

2005

"Multidimensional Coherent Vibrational Spectroscopy; Femtosecond Snapshots of Molecular Dynamics", Hong Kong University of Science and Technology, Hong Kong, China, January 3-7, 2005.

"Multidimensional Coherent Vibrational Spectroscopy; Femtosecond Snapshots of Molecular Dynamics", French-Israeli Symposium on Non-linear & Quantum Optics, Ein Bokek, Israel, February 20-25, 2005.

"Multidimensional Coherent Vibrational Spectroscopies of Peptides; Femtosecond Snapshots of Structure and Dynamics", Chemical Physics Colloquium, University of Colorado, Boulder, CO, March 3-4, 2005.

"Multipoint Correlation Functions and Liouville Space Pathways in Single Molecule Spectroscopy", Workshop on Single Molecule Research in the New Millennium, Department of Energy, Rockville, MD, April 10-12, 2005.

"Multidimensional Coherent Vibrational Spectroscopy; Femtosecond Snapshots of Molecular Dynamics ", Twelfth International Conference on Time-Resolved Vibrational Spectroscopy, National Institute of Standards and Technology (NIST), Gaithersburg, MD, May 23-27, 2005.

"Multidimensional Coherent Vibrational Spectroscopy of Peptides: Femtosecond Snapshots of Structure and Dynamics", Chemical Physics Seminar, California Institute of Technology, Pomona, CA, May 31, 2005.

UCOP Forum on High Energy Density Science and Ultrafast Science, Pleasanton, CA, June 13-14, 2005.

American Conference of Theoretical Chemistry Conference, University of California, Los Angeles, July 16-21, 2005.

University of Oregon, Oregon Center for Optics, "Multidimensional Coherent Vibrational Spectroscopy; Femtosecond Snapshots of Molecular Dynamics" September 8-9, 2005.

"Theory and Simulations of Ultrafast Nonlinear X-ray Spectroscopy of Molecules", 2005 DOE Atomic, Molecular and Optical Sciences Research Meeting, Airlie Conference Center, Warrington, VA, September 12-15, 2005.

"Coherent Vibrational Analogues of Multidimensional NMR; Femtosecond Snapshots of Peptide Dynamics", Frontier in Chemistry Lecture, Wayne State University, October 31, 2005.

"Coherent Femtosecond Multidimensional Spectroscopy of Vibrational Excitons in Proteins", Molecular Nanoscience Workshop, A symposium in honor of Dr. Chemla's 65th Birthday, Berkeley, CA, November 21, 2005.

"Chirally sensitive nonlinear spectroscopy of molecules", Symposium on Space and Time-Resolved Molecular Reaction Dynamics and Spectroscopy, PacificChem Meeting, Honolulu, HI, December 15-20, 2005.

"Multidimensional Coherent Vibrational Spectroscopy; Femtosecond Snapshots of Molecular Dynamics", Symposium on Photophysical Dynamics in Biological Molecules, PacificChem Meeting, Honolulu, HI, December 15-20, 2005.

2006

"Nonlinear Ultrafast X-ray Spectroscopy: Theoretical Challenges", Workshop on Pump and Probe Experiments at the European X-Ray Free-Electron Laser (XFEL), Copenhagen, January 20-21, 2006.

"Probing the Structure and Dynamics of Peptides by Multiple Laser Pulses: Femtosecond Analogues of Multidimensional NMR", Physics & Theoretical Colloquia Series, Los Alamos National Laboratory, January 26, 2006.

"Probing the Structure and Dynamics of Peptides by Multiple Laser Pulses: Femtosecond Analogues of Multidimensional NMR", University of Kyoto, Department of Chemistry seminar Japan, Feb. 18, 2006.

"Probing the Structure and Dynamics of Peptides by Multiple Laser Pulses: Femtosecond Analogues of Multidimensional NMR", University of Nagoya, Department of Chemistry seminar, Japan, Feb. 20, 2006

"Probing the Structure and Dynamics of Peptides by Multiple Laser Pulses: Femtosecond Analogues of Multidimensional NMR, IMS in Okazaki, Explanation of Nature by Numerical Stimulation, Japan, Feb, 2006.

"Ultrafast Molecular Spectroscopy", Asian Winter School in Okazaki, Explanation of Nature by Numerical Stimulation, Japan, Feb 20-23, 2006.

"Fluctuation theorems in quantum systems", Work, Dissipation and Fluctuations in Nonequilibrium Physics, Brussels, March 22-25, 2006

"Hybrid Qm/Mm Simulation Protocols For Coherent Multidimensional Spectra Of Peptides", Quantum Molecular Dynamics in the Condensed Phase: Towards bridging the Gap between Theory and Experiment, American Chemical Society, Atlanta, March 26-30, 2006.

"Probing Molecular Structure and Dynamics by Coherent Nonlinear Spectroscopy: Femtosecond Analogues of Multidimensional NMR", Lund University, Lund, March 27, 2006.

"Nonlinear Ultrafast X-Ray Spectroscopy at the XFEL" Uppsala University, Sweden, March 29, 2006.

"Probing Molecular Structure and Dynamics by Coherent Nonlinear Spectroscopy: Femtosecond Analogues of Multidimensional NMR", Royal Institute of Technology (KTH), Stockholm, March 30, 2006.

49^{ers}, Vilnius, Lithunia, May 5-8, 2006.

"Challenges in Chemical Physics: Single Molecules, Complex Systems and Anomalous Statistics", Tel Aviv University, May 21-22, 2006.

International seminar and workshop on Non-Equilibrium Dynamics in Interacting Systems (NEQDIS), Dresden, April 18-May 5, 2006

ITAMP, "X-ray-free electron lasers: challenges for theory, Cambridge, MA, June 19-21, 2006.
Visiting professor in Vienna, "The Principle's of Nonlinear Optical Spectroscopy", University of Vienna, June 2006.

15th International Conference on Ultrafast Phenomena, Monterey, CA, July 31-August 4, 2005.

"Probing the Structure and Dynamics of Peptides by Multiple Laser Pulses: Femtosecond Analogues of Multidimensional NMR", 20th International Conference of Raman Spectroscopy (ICORS), Japan, August 20-25, 2006.

AMOS, DOE contractors meeting, Airlie Conference Center, Warrington, VA, Sept 10-16, 2006

ACS Symposium entitled Fifty Years of Electron Transfer and RRKM Theories, San Francisco, CA, Sept 10-14, 2006

JILA Distinguished Visitors Program, 2006.

Consultative and advisory functions:

None

Transitions. Describe cases where knowledge resulting from your effort is used, or will be used, in a technology application.

None

New discoveries, inventions, or patent disclosures. (If None, report None.)

None

Honors/Awards: List honors and awards received during the grant/contract period. List lifetime achievement honors such as Nobel Prize, honorary doctorates, and society fellowships prior to this effort.

2002	Sackler Professor by Special Appointment, Tel Aviv University
2003	Lippincott Award, The Optical Society of America
2003-	Chancellor Professor of Chemistry, University of California at Irvine
2003-	Associate Faculty Lawrence Berkeley National Lab, Berkeley, CA